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Synthesis and crystal structures of metal complexes of 4-chloro-and 2,4 dichlorophenoxyacetic acid

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ABSTRACT

Today, in a period of global climate change and environmental problems, the world is experiencing a decline in the productivity of agricultural crops. The need for effective chemical compounds that control the growth of cultivated plants and increase their productivity is increasing. In world agriculture, obtaining stimulants that are low in toxicity and highly effective, increasing plant productivity and combating various harmful insects and phytopathogenic microorganisms are important issues. It is known that 4-chlorophenoxyacetic (4-D) and 2,4-dichlorophenoxyacetic (2,4-D) acids are widely used in agriculture as herbicides and plant growth stimulants. 2,4-D, which is considered a systemic herbicide, moves easily in the plant body together with nutrients and metabolic products and leads to general poisoning (deformation of plant stems and leaves, their brittleness, growth retardation). This is an important factor in controlling perennial weeds with a well-developed root system. Contact and systemic herbicides are sprayed on the surface of the plant leaf, as well as introduced into the soil. 2,4-D has a selective effect mainly on dicotyledonous weeds, so it is widely used in monocotyledonous crop fields. On the basis of these compounds, many studies have been conducted on the synthesis of highly biologically active complex compounds and the study of their molecular and crystal structures and the determination of their mechanism of action. As a rule, these compounds exhibit herbicidal properties in high concentrations, but in microconcentrations (less than 0.001%) they serve as plant growth accelerators (stimulants).

1. Synthesis, molecular and crystal structures of 4-chlorophenoxyacetic acid complex compounds

Chlorphenoxy herbicides are known to be one of the most common pesticide families. In addition, they are synthetic auxins used for weed control in corn, rice, and wheat fields [1,2]. Despite the forms introduced into the environment (free acids, salts and esters of alkaline and amino acids), they retain their pesticidal activity. They stay in the soil for about 1 month [3] remains and dissolves well in water. In the soil, they can bind with metal ions such as Cu(II), Co(II), Ni(II) [4]. Flexible ligands of organic carboxylic acids have high deformation, a wide range of configurations and conformations, and have good opportunities for the synthesis of coordination compounds with new structures and functions [5-9].

4-chlorophenoxyacetic acid is one such compound, whose biological activity has been widely studied [10]. Vibrational and electronic spectra of some phenoxyacetic acid herbicides were studied only by DFT method [11]. Single crystals of the complex combination of 4-D with copper(II) ions $[Cu(4\text{-}D)_2(H_2O)_2]$ were grown and spatial structure was studied using RSA in Scheme 1. [12]. Although 4-D and TEA were added to the aqueous solution of $Ni(CH_3COO)_2 \cdot 4H_2O$ crystal hydrate in order to obtain a mixed ligand complex of Ni(II), as a result of

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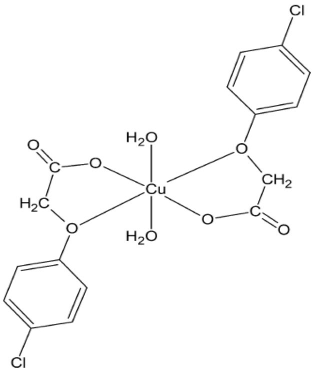
the experiment, a complex compound with the composition $[Ni(4\text{-}D)_2(H_2O)_4]$ was formed was determined to be Figure 1. [13]



Scheme 1. The structure of the complex compound $[Cu(4\text{-}D)_2(H_2O)_2]$.

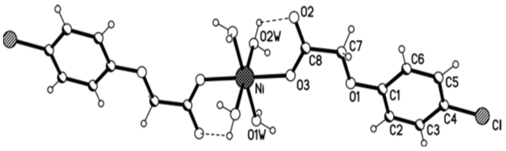


Fig. 1. Molecular structure and numbering of atoms of the complex compound $[Ni(4\text{-}D)_2(H_2O)_4]$. (Dotted line indicates intramolecular hydrogen bond)

The complex is composed of separate molecules with neutral $[Ni(4\text{-}D)_2(H_2O)_4]$ composition, and the Ni^{2+} cation forms a slightly deformed tetragonal bipyramidal NiO_6 polyhedron located in the center of crystallographic symmetry. In the equatorial plane of the bipyramid there are O atoms of 4 water molecules, and in the apical positions there are O atoms of the carboxylate group of two 4-D ligands. The equatorial bond lengths of Ni−O1W and Ni−O_2W in the complex are 2.038(4), 2.081(4) Å, respectively, and the axial bond length of Ni–O_3 is 2.063(4) Å. In the crystal, intramolecular and intermolecular hydrogen bonds of the O-H···O type were formed between H_2O molecules and the non-coordinating O atom of the carboxylate group.

In the crystals of the $[Ni(4\text{-}D)_2(H_2O)_4]$ complex, a chain oriented along the b axis is formed due to hydrogen bonds of the O-H···O type, and the chains, in turn, are formed by two hydrogen bonds of the other O H···O type it was determined to form a dimensional layer. When the molecules in the crystals of the $[Ni(4\text{-}D)_2(H_2O)_4]$ complex are located at a distance of 4.894, 5.769, 7.107 Å, their interaction energies were found to be -57.0, -17.9, -16.0 kJ/mol, respectively Figure 2.

Mixed-ligand chelate compounds of Co^{2+} and Cu^{2+} ions with 4-D and MEA composition $[Co(4\text{-}D)_2(MEA)_2]$ and $[Cu(4\text{-}D)_2(MEA)_2]$ were synthesized. The complex compounds $[Co(4\text{-}D)_2(MEA)_2]$ and $[Cu(4\text{-}D)_2(MEA)_2]$ have an isostructural crystal structure and are composed of discrete molecules. Coordination polyhedra of So and Cu atoms–deformed octahedron N_2O_4, 4-D ligand carboxylate groups formed by two O atoms, and MEA molecule formed by two O atoms and two N atoms, located in the crystallographic centers of symmetry. In $[Cu(4\text{-}D)_2(MEA)_2]$ complex, equatorial Cu–O(2) and Cu–N(1) bond lengths are 2.025(6), 1.964(6) Å, respectively, axial Cu–O(4) length is equal to 2.590(7)Å, its significant length is explained by Jan-Teller effect Figure 3.

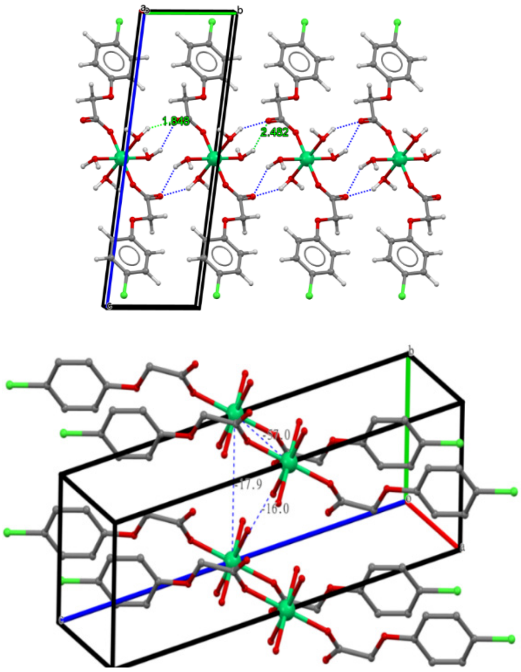


Fig. 2. O-H···O type intermolecular hydrogen bonds and intermolecular interaction energy of the complex compound $[Ni(4\text{-}D)_2(H_2O)_4]$

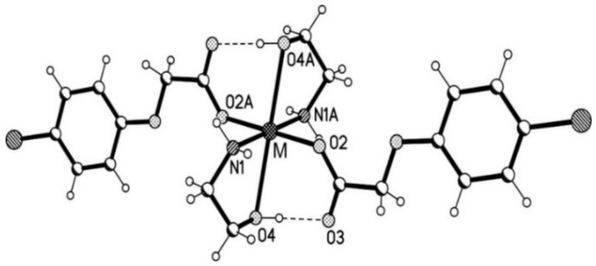


Fig. 3. Molecular structures of [Co(4-D)2(MEA)2] and $[Cu(4\text{-}D)_2(MEA)_2]$ complexes

A trinuclear mixed-valent oxo-center complex of manganese was synthesized: $[Mn_3O(4\text{-}D)_6L_3]$ (L= 3-methylpyridine or water). For this, N-n-Bu4MnO4 was reacted with appropriate reagents in ethanol and 3-methylpyridine. In the crystal, the oxo-center is Mn3O, and the bridging carboxylate and terminal 3-methylpyridine groups are involved as peripheral ligands, the whole cluster has an almost third-order symmetry axis [14].

The parameters of the unit cell of the triclinic crystal are as follows: space group R1, a=15.344(3) Å, b=15.990(3) Å, c=16.801(3) Å, a=65.03(3)o, b=80.26(3)° ,g=70.68(3)o,V=3524.3(11)Å3, Z=2.

2. Synthesis, molecular and crystal structures of 2,4-dichlorophenoxyacetic acid complex compounds

A mixture of 2,4-D (0.2 mmol), $CoCl_2$ (0.1 mmol) and 2,2'-bipyridine (0.2 mmol) was dissolved in 15 mL methanol/water (3:1, v/v) solvent. A triethylamine solution was added dropwise to the obtained reaction mixture until the pH was 6.5. The reaction was heated in a water bath at 333 K for 28 h. It was then filtered and the filtrate was slowly cooled to room temperature. Red single crystals suitable for RSA were grown for three weeks. $C_{16}H_{22}Cl_4CoO_{12}$, monoclinic, space group P21/n , a=6.754(2)Å, b=5.300(1)Å, c=33.456(8)Å, b=92.430(4)°, V=1196.5Å3, Z=2 , Rgt(F)=0.050, wRref(F2)=0.110, T=294 K. The central So(II) ion formed a distorted octahedron in coordination with 6 oxygen atoms [15]. 2 of them belong to 2 2,4-D molecules, 4 belong to water molecules Figure 4.

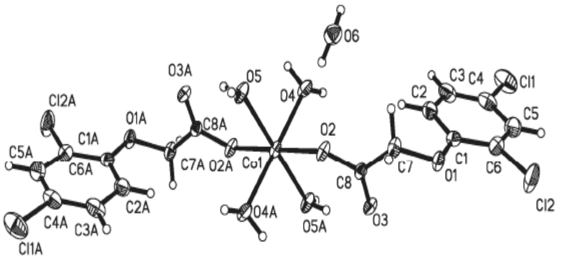
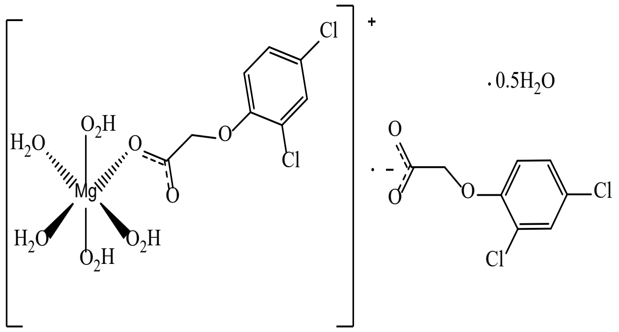


Fig. 4. Molecular structure of the complex compound $[Co(2,4\text{-}D)2(H_2O)_4]H_2O$

CoO_6 is a unit, O_2, O_4, O_2A and O_4A atoms are located in the equatorial plane, and O_5 and O_5A occupy the axial position. The bond angles O_2–Co_1–O_4, O4–Co1–O2A, O_2A–Co1–O_4A and O_4A–Co1–O_2 are: 87.94(11)°, 92.06(11)°, 87.95(11)° and is 92.05(11)° and the sum is 360°. Co–O bond lengths formed by water molecules with oxygen atoms are different.

The synthesis of the complex of the 2,4-D ligand with the Mg^{2+} cation was carried out as follows: an abundant amount of MgCO3 was added to a mixed solution of 2,4-D (0.1 mmol) in ethanol-water (1:10 by volume), and after intensive stirring and heating, the excess MgCO3 was filtered off. The filtrate was slowly evaporated at room temperature to grow colorless prismatic single crystals. According to the results of RSA, the complex has the composition $[Mg(2,4\text{-}D)(H_2O)_5]\cdot(2,4\text{-}D)\cdot0.5H_2O$ scheme 2[16]. In this case, the bidentate 2,4-D ligand is simultaneously included in the complex cation and located in the outer sphere in Scheme 2. It has been determined that O··H···O type internal and intermolecular H-bonds are formed in the crystal. All coordinated and free water molecules participate in hydrogen bonds, and carboxylate anions form a layer parallel to the (001) plane with the O acceptor atom. Between these layers, there are 2,4-D ligand-anions A···Bi intercenter symmetric p-p [minimum inter-ring distance of 3.6405(17) Å and short O—H···Cl interactions (Figure 5).



Scheme-2. Structure of the complex compound $[Mg(2,4\text{-}D)(H_2O)_5](2,4\text{-}D)\cdot0.5H_2O$

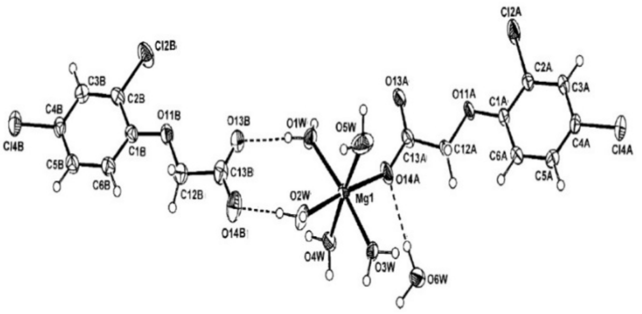


Fig. 5. Molecular structure and atomic numbering of the complex compound $[Mg(2,4\text{-}D)(H_2O)_5](2,4\text{-}D)\cdot0.5H_2O$. (Hydrogen bonds are indicated by dotted lines)

In order to obtain a complex compound containing Fe(II) cation, a mixture of $FeCl_2$ salt (1 mmol), ligand 2,4-D (1 mmol), NaOH (1 mmol) and water (10 ml) was mixed for 20 minutes, then 20 ml of Teflon coated was left for two days in an autoclave with a steel container heated at 433 K. Red blocky crystals were then obtained upon cooling to room temperature at a rate of 5 K/h.

In the complex compound $[Fe(2,4\text{-}D)2(H_2O)_2]n$, the iron(II) atom is located in the center of inversion [17]. The central iron atom in the complex is coordinated with 4 O atoms and 2 water molecules of 4 2,4-D ligands and has a distorted octahedral geometry. Carboxyl groups of 2,4-D ligands were attached to Fe atoms and formed a polymer layer in the bc plane Figure 6.

Hydrogen O···H···O bonds between the layers ensured the stability of the two-dimensional structure. These monoclinic crystals belong to the P21/c space group, with other cell dimensions as follows: α = 17.604(2) Å, β = 7.3122(8) Å, c = 8.0312(9) Å, β = 94.258(2)°, V = 1031.0 (2) Å3, Z = 2, wR(F2) = 0.097, T = 296 K. The distance between neighboring atoms Fe···Fe is 5.431(4) Å.{[Co(2,4-D)2(μ2- The complex compound $H_2O)(H_2O)_2]$ $\cdot(H_2O)_2\}n$ was synthesized under hydrothermal conditions, its structure was studied by elemental analysis, IR-spectroscopy, thermogravimetric analysis and X-ray diffraction methods scheme 3[18].

This complex has a 1-D chain crossed by So and bridging water molecules, with a Co···Co distance of 4.028(2) Å. The dimensions of the unit cell of the crystal are as follows: space group Pna21, a=8.0559(4) Å, b=8.0553(4) Å, c=37.139(2)Å, a=b=g=90° (Figure 6).

In the complex, the 2,4-D ligand is monodentately coordinated to Co^{2+} cations, forming a polymer-type complex through water molecules. $\{[Co(2,4\text{-}D)2(\mu 2\text{-}H_2O)(H_2O)_2]^*(H_2O)_2\}n$. Weak antiferromagnetic effects were detected in the complex.

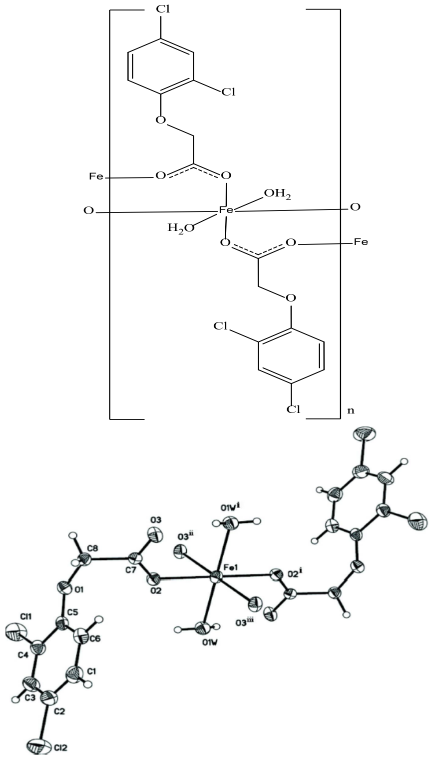
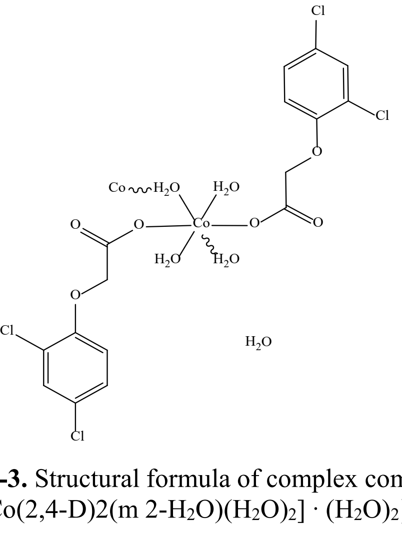


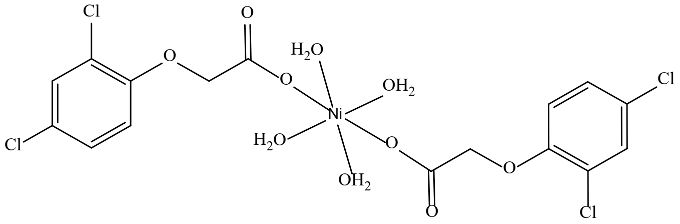
Fig. 6. Structural formula, molecular structure and two-dimensional view of crystals of the complex compound $[Fe(2,4\text{-}D)_2(H_2O)_2]n$.



Scheme-3. Structural formula of complex compound $\{[Co(2,4\text{-}D)2(m\ 2\text{-}H_2O)(H_2O)_2] \cdot (H_2O)_2\}n$

Monoclinic, space group R21/c, a = 16.860(3) Å, b = 8.1370(16) Å, c = 8.3010(17) Å, b = 95.87(3)°, V = 1132.8(4) Å, Z = 2, Rgt(F) = 0.071, wRref(F2) = 0.214, T = 293 K. To synthesize the complex, a 2:1 mol ratio mixture of 2,4-D and $NiCl_2 \cdot 6H_2O$ was stirred in methanol for 3 hours. Then, when the filtrate was kept in air for 7 days, green block-shaped single crystals were formed [19,20].

In the $[Ni(2,4\text{-}D)_2(H_2O)_4]$ complex, the Ni(II) atom has slightly distorted octahedral NiO6 coordination. Two of them are monodentate 2,4-D ligand and O atoms of 4 water molecules. Its conformation is stable due to intramolecular O··H···O hydrogen bonds. There are also intermolecular O··H···O hydrogen bonds Scheme 4.



Scheme 4. $[Ni(2,4\text{-}D)_2(H_2O)_4]$ complex compound structure

Complexes of Co(II), Ni(II) and Cu(II) metals with 2,4-D were synthesized and their structure was described. The geometry of the metal-ligand interaction was investigated by XAFS and DFT methods. In the coordination sphere of $[Co(2,4\text{-}D)_2 \cdot 6H_2O]$ and $[Ni(2,4\text{-}D)_2 \cdot 4H_2O]$ complexes in octahedral geometry, there are two carboxylate groups of 2,4-D anions and 4 water molecules. In the $[Cu(2,4\text{-}D)_2 \cdot 4H_2O]$ complex, a flat square geometry is formed around the metal cation due to two monodentate ligand carboxylate groups and two water molecules [21]. In the IR-spectrum of 2,4-D ligand, broad absorption lines in the region of 2600–3100 cm^{-1} correspond to valence vibrations of C–H and O–H bonds. In metal complexes, this part of the IR spectrum expands to 3600 cm^{-1}. This is due to the presence of water molecules in the complexes and is consistent with elemental analysis and gravimetric data. The FTIR spectrum of the ligand and the complex is almost similar in the region of 1000–1800 cm^{-1}, the difference is observed only in the absorption characteristic of the carboxyl group. This proves that the metal-ligand bonds are formed through the carboxylate O atom, and simple ether oxygen and chlorine atoms are not involved in the bonds. Absorption lines specific to the –COOH group in the 2,4-D molecule consist of carbonyl C=O group valence vibrations (1728 cm^{-1}) and C–O(H) group specific absorptions in the 1310 cm^{-1} region. Due to the deprotonation of the carboxyl group and its participation in the formation of the complex, two strong absorptions characteristic of the carboxylate anion occur, asymmetric and symmetric bond vibrations. In these complexes, these absorptions are observed in the regions 1630–1588 cm^{-1} and 1344–1339 cm^{-1}, respectively. The low intensity of the optical absorptions indicates that the space around the intermediate metal atom is almost symmetrical to the center, being octahedral or square. In this case d-d transitions are symmetry forbidden. Therefore, 2,4-D anions participate as monodentate ligands in these complexes [21].

As a result of the reaction of 2,4-D with $CuSO_4 \cdot 5H_2O$

crystal hydrate in an ethanol-water solution, a neutral, mononuclear complex with the composition $[Cu(2,4\text{-}D)_2(H_2O)_3]\cdot 3,18H_2O\cdot S2N6O$ was obtained [22]. There are no symmetry elements in the complex. Two 2,4-D anions are coordinated to the central Cu^{2+} ion through O atoms of the carboxyl group (O_2, O_2V) in the monodentate state and 3 water molecules coordinated to O atoms (O1W, O2W, O3W). The coordination polyhedron formed a deformed tetragonal pyramid. In the outer coordination sphere, one ethanol and 4 water molecules are localized due to N-bonds. The multiplicity of O7W water molecule is equal to 0.18.

This $[Cu(2,4\text{-}D)_2(H_2O)_3]\cdot 3,18H_2O\cdot C_2H_6O$ complex with water, ethanol and 2,4-D molecules is parallel to the bc plane due to O−H···H hydrogen bonds the formation of a two-dimensional layer was determined, and it was noted that the crystal system is stable due to the interactions of N-bonds and molecules of other nature Figure 7.

The value of the Cu−O bond length lies in the range of 1.938−2.362 Å. Oxygen atoms O_2 (SOO−), O_2V (SOO−), O1W (H_2O) and O_3W (H_2O) are located at the nodes of the base of the tetragonal pyramid; Su−O coordination bond lengths are 1.938, 1.965, 1.936, and 1.923 Å, respectively, and the oxygen atom of O2W (H2O) at the top of the pyramid is at a distance of 2.345 Å, and this value is explained by the Jan-Teller effect Figure 8.

The polymer type [Zn(2,4-D)2]n complex was synthesized from the reaction of a 1:2 mol ratio mixture of $ZnCl_2$ and 2,4-D and sodium hydroxide under hydrothermal conditions (pH=7.0) Scheme 5.

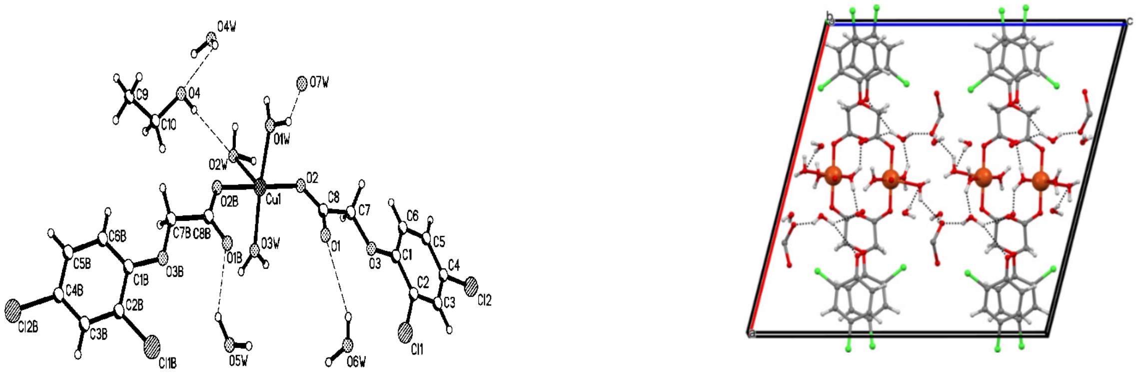
Zn(II) atom formed a distorted tetrahedron in coordination with O atoms of 4 monodentate 2,4-D ligands. Each ligand is a bridge between two Zn(II) atoms, forming a polymer chain along the α axis. Between adjacent chains there are N-bonds of the C··H···Cl type [23]. The crystals are monoclinic and belong to space group R1, a= 4.7322(10) Å, b=10.459(2) Å, c=18.979(4) Å, a=79.340(2)°, b=89.838(2)°, = 82.847(3)°, V = 915.8(3) Å3, Z = 2, Rgt(F) = 0.030, wRref(F2) = 0.091, T=296 K. Also, complexes of Zn(II) and Cd(II) with 2,4-D were synthesized in a water-methanol mixture and their structure was studied by elemental analysis, IR-spectrum, mass-spectrum thermal analysis. In Zn(II) salts, the alcohol molecule tends to enter the complex, while in Cd(II) salts, such a situation is not observed. Only in aqueous medium, Zn(II) salts are normally $[Zn(H_2O)_4(2,4\text{-}D)_2]\cdot[Zn(H_2O)_2(2,4\text{-}D)_2]$ [24; 243–247-b] and in hydrothermal conditions $[Zn(2,4\text{-}D)_2]n$ [23] forms complexes.

The synthesized $[Zn(2,4\text{-}D)_2(en)]$ complex was analyzed by X-ray crystallographic techniques. The asymmetric unit of the title compound consists of a mononuclear complex of the formula $[Zn(C_8H_5Cl_2O_3)_2(C_2H_8N_2)]$, as shown in Figure 8.

The molecular structure of compound is crystallized in the monoclinic space group *P*2/c with neutral charges. The central Zn^{2+} ion in the complex compound is coordinated in the 2,4-D monodentate way while the ethylenediamine (en) ligand coordinates in a bidentate state. The coordination of the Zn(II) cation is a tetrahedron defined by an N_2O_2 coordination set and is hybridized in the sp^3 state with a coordination number of 4 (Table 1). The bond lengths of the complex are included in the Table 2.

Table 1. Bond Distances (Å) of $[Zn(2,4\text{-}D)_2EDA$

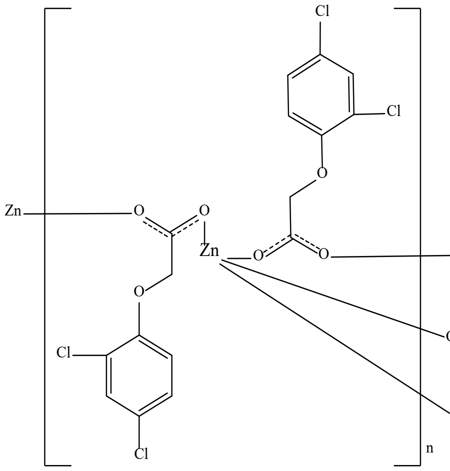
Bond	Distances (Å)
Zn1−O1	1.940(3)
Zn1−N1	2.038(5)
Zn1−O1 ^{i}	1.940(3)
Zn1−N1 ^{i}	2.038(5)



a

b

Fig 7. $[Cu(2,4\text{-}D)_2(H_2O)_3]\cdot 3,18H_2O\cdot C_2H_6O$ complex compound molecule structure and atom numbering. (Hydrogen bonds are indicated by dotted lines)



Scheme-5. [Zn(2,4-D)2]n, complex compound structure

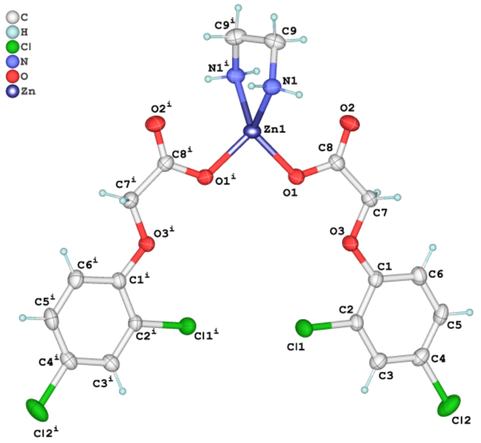


Fig. 8. Molecular structure of the complex [Zn(2,4-D)$_2$En]

This tetrahedral coordination around Zn(II) contrasts with the octahedral environments commonly observed for Ni(II) and Co(II) 2,4-D complexes reported in the literature. The preference of Zn(II) for CN = 4 can be attributed to its d^{10} electronic configuration, which lacks ligand field stabilization in octahedral fields, whereas Ni(II) (d^8) and Co(II) (d^7) benefit from higher LFSE in octahedral geometries. Therefore, the observed geometry trend reflects intrinsic electronic factors of the metal ions, modulated by steric effects of the chlorinated phenoxyacetate ligands. This situation is explained as a postulate as follows: Zn salts are connected with hydroxyl groups present in the membranes and enzymes of living organisms, while Cd salts exist in the form of separate complex molecules in the fluids of living organisms.

The crystal structure of tetraaqua-bis(2,4-dichlorophenoxyacetato)zinc(II)-diquabis-(2,4-dichlorophenoxyacetato)zinc(II) is orthorhombic and belongs to the space group Pna21. The crystal cell contains 4 molecular dimers, a =19.302(2) Å, b=6.051(1) Å, c=36.325(6) Å, V=4242.7 Å3, Z=4. The unit cell of the complex {[(Zn(H$_2$O)$_4$(2,4-D)$_2$][Zn(H$_2$O)$_2$(2,4-D)$_2$]} consists of two discrete and stereochemically different complexes, one of which is octahedral around the zinc center. , the other is tetrahedral. The coordination of the first zinc is six, due to the 4 oxygens of the aqua ligands [ZnO, 2.069(10)-2.147(9) Å] and two carboxyl groups of the monodentate 2,4-D ligands in the trans-state [Zn··O , 2.071(9), 2.121(9) Å] was formed [24].

The crystal structure of the complexes was studied by RSA [25]. [Zn(2,4-D)$_2$(MeOH)$_2$]n, monoclinic, space group P21/c, a=19.094 Å, b=7.378 Å, c=8.008 Å, a=90.00o, b=101.134o, =90.00o, V=1106.95 Å3 Figure 8. [Cd(2,4-D)$_2$(H$_2$O)$_2$]n, monoclinic, space group P21/c, a=17.730 Å, b=7.293 Å, c=8.060 Å, α=90.00o, b=95.18o, α =90.00o, V=1037.9 Å3 Figure 9.

The sizes of this [Cd(2,4-D)$_2$(H$_2$O)$_2$]n complex obtained by other authors are as follows: monoclinic, space group P21/c, *a* =17.732(4) Å, *b*=7.2796(15) Å , *c*=8.0624(16) Å, b=95.20o, V=1036.4(4) Å3, Z=2, T=295K. The Cd(II) atom is in the inversion center and has a partially distorted octahedral coordination. Each Cd(II) atom is six-coordinated, 4 of which are carboxyl group O atoms, belonging to 2,4-D ligands of different symmetry [Cd-O distance 2.274 (2) Å] and 2 water molecules are O atoms. The oxyacetate group is out of the plane of the benzene ring, the C_3-O_3-C_2-C_1 torsion angle is -82.0(2)o. C-O bond lengths of the carboxyl group (2.2703-2.3325 Å) prove that it is deprotonated and the double bond is delocalized [26]. Inorganic crystalline hydrate Cd(NO$_3$)$_2$·4H$_2$O and Pb(NO$_3$)$_2$ salts are mixed with 2,4-D ligand in a 1:2 mol ratio in a neutral environment, and the composition is [Pb(2,4-D)$_2$·H$_2$O] and [Cd(2,4-D)$_2$·2H$_2$O] complexes were obtained.

$$2(2\;4-D)+M^{2+}+nH_2O\xrightarrow{-2H^+}M(2\;4-D)_2\bullet nH_2O$$

The solubility of [Cd(2,4-D)$_2$·2H$_2$O] and [Pb(2,4-D)$_2$·H$_2$O] complexes in water at room temperature was found to be 4.96 and 0.35 mol/l, respectively. Their powder RSA, IR-spectrum and electrical conductivity were studied [27]. The Ni(II) complex recrystallized from DMFA is binuclear, and it was observed that the carboxylate groups of 2,4-D act as a bridge in its "Chinese lantern" structure [28]. This complex crystallized in the triclinic $P\bar{1}$ space group, *a*=7.630(2)Å, *b*=9.914(2)Å, *c*=16.585(3)Å, *a*=95.72(2)º, *b*=99.13(2)º, g= 92.73(2)º, V=1229.9(4)Å3 and Z = 1. The asymmetric part of the crystal lattice contains one nickel cation, two 2,4-D anions, and one DMFA molecule. When this part of the crystal is transformed around the center of symmetry, a binuclear complex is obtained (Figure 10).

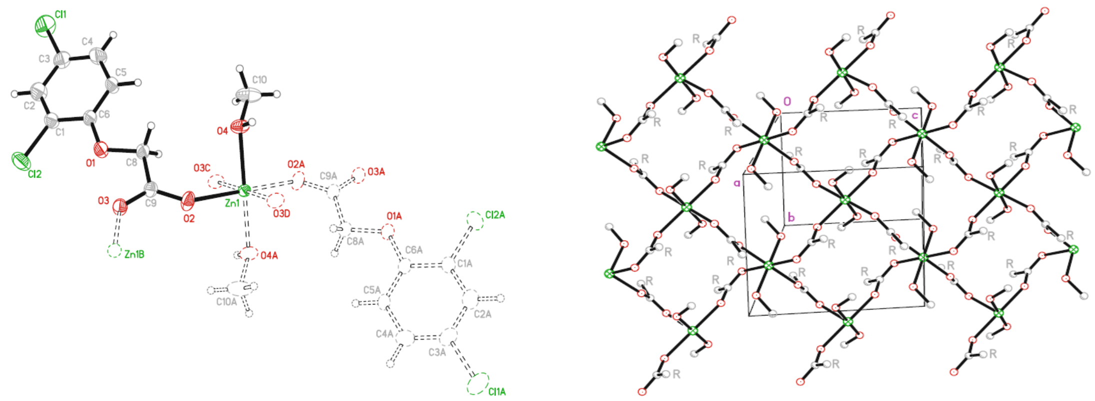


Fig. 9 [Zn(2,4-D)$_2$(MeOH)$_2$]n complex compound structure and arrangement of molecules in the crystal lattice

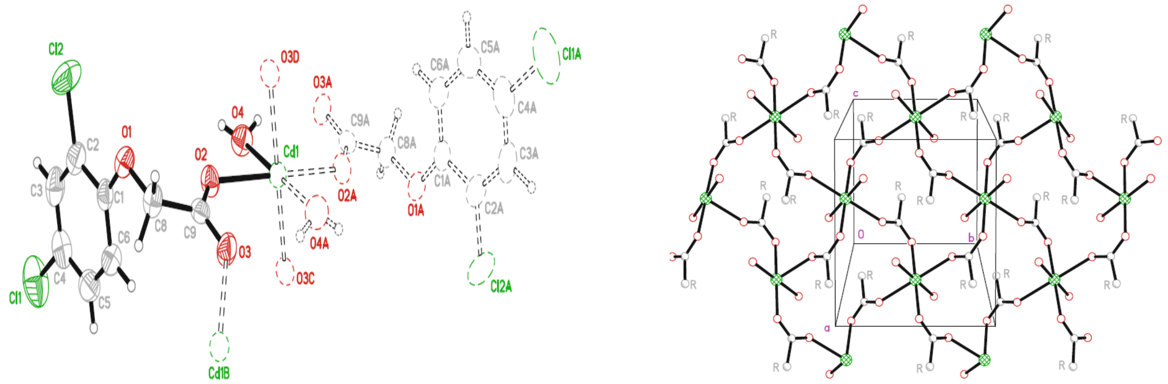


Fig. 10. [Cd(2,4-D)$_2$(H$_2$O)$_2$]n complex compound structure and arrangement of molecules in the crystal lattice

The complex consists of discrete dinuclear cations, 2,4-D counterions, and free water molecules, which are assembled into a structural matrix due to dimethylbipyridine ligands and N-bonds with π···π effect Figure 11.

Binuclear Ni_2O_{10} in the center, the upper part is built at the expense of the O atom of the DMFA molecule, while the base consists of 4 bridging oxygen atoms of the carboxylate groups of 2,4-D anions Figure 12.

A tetragonal pyramid is formed around the Ni cation. Ni–O bond lengths range from 1.954(2) to 2.123(2) Å, the longest of which is Ni–O(solvent). Ni–Ni bond length is 2.649(9) Å [21] (Table 2).

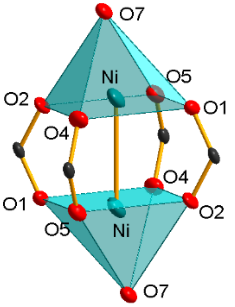
The complex containing [Mn_2(2,4-D)3(DMPY)2(μ2-H_2O)(H_2O)](2,4-D)*0.2(H_2O) was synthesized under hydrothermal conditions, elemental analysis, IR- The structure was studied by spectroscopy, thermogravimetric analysis and X-ray diffraction methods [18]. The unit cell parameters of the crystals of the mixed ligand complex formed by the copper(II) cation with 2,4-D and 2,2-bipyridine (BP) are as follows: space group C2/c, α=39.686(8) Å, β=7.1543 (14) Å, c=19.578(4) Å, b=102.46(3)°, V= 5427.77 Å3, Z=8, Rgt(F) =0.039, wRref(F2) =0.094, T =113 K Figure 13.

A mixture of copper(II) carbonate (0.19 mmol), 2,4-D (0.58 mmol) and 2,2'-bipyridine (0.13 mmol) was dissolved in 15 mL of 95% ethanol. The pH value of the obtained reaction mixture was adjusted to 4.8 by adding one drop of triethylamine solution. The reaction mixture was kept in a water bath at a temperature of 343 K for 20 hours. The mixture was then filtered, and the filtrate was slowly cooled to room temperature. Blue block-shaped single crystals were obtained after one week.

The [Cu(2,4-D)$_2$(BP)H_2O] complex formed by Cu^{2+} with 2,4-D, BP and water molecules is mononuclear and has a neutral structure, $C_{26}H_{20}Cl_4CuN_2O_7$, monoclinic. The copper atom is coordinated in a deformed pyramid type (CuN_2O_3). Cu(II) cation is coordinated with two molecules of BP as N,N' bidentate and 2 2,4-D anions as monodentate ligands through oxygen atoms [28]. In the crystal, Su(1)-N(1), Cu(2)-N(2), Cu(1)-O(3), Cu(1)-O(4) and Cu(1)-O(H_2O) distances are 2.004(2), 1.989(2), 1.941(2), 1.951(2), and 2.306(2) Å, respectively.

Reaction of a mixture of copper(II) nitrate $Cu(NO_3)_2$*$5H_2O$ with 4,4-bipyridine and 2,4-D in 1:1:2 mol ratio under solvo-thermal conditions (heating in an autoclave at a temperature of 403 K, 2 days, ethanol) as a result, a yellow complex containing {[$Cu_2(C_8H_5Cl_2O_3)(C_{10}H_8N_2)_2$]$NO_3$}n was obtained [29]. Each of the copper(I) atoms in the asymmetric unit is three-coordinated to two N atoms of the two 4,4-bipy ligands and one O atom of the 2,4-D ligand.

Table 2. Bond lengths and angles in the $[Ni_2(2,4\text{-}D)_4(DMFA)_2]$ complex

Ni–O/Ni (Å)		O–Ni–O (°)		
Ni–O1	1.954(2)	O1–Ni–O5^{i}	88.9(1)	
Ni–O2^{i}	1.978(2)	O1–Ni–O2^{i}	168.0(1)	
Ni–O4	1.981(2)	O5^{i}–Ni–O2^{i}	87.6(1)	
Ni–O5^{i}	1.975(2)	O1–Ni–O4	89.5(1)	
Ni–O7	2.123(2)	O5^{i}–Ni–O4	168.5(1)	
Ni–Ni^{i}	2.649(9)	O2^{i}–Ni–O4	91.6(1)	
		O1–Ni–O7	100.2(1)	
		O5^{i}–Ni–O7	96.6(1)	
		O2^{i}–Ni–O7	91.6(1)	
		O4–Ni–O7	94.9(1)	

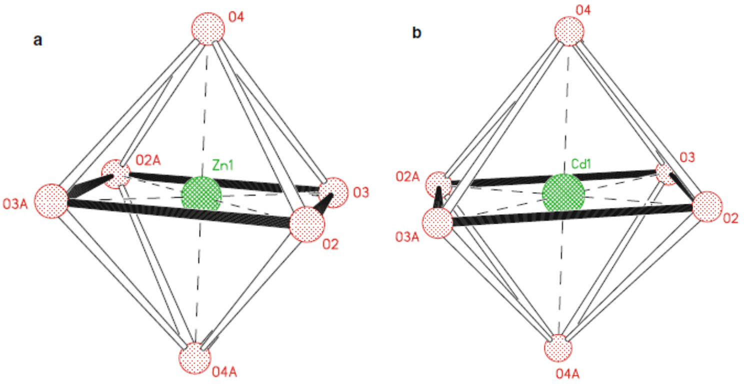


Fig. 11. Coordination in complex compounds $[Zn(2,4\text{-}D)_2(MeOH)_2]n$ and $[Cd(2,4\text{-}D)_2(H_2O)_2]n$

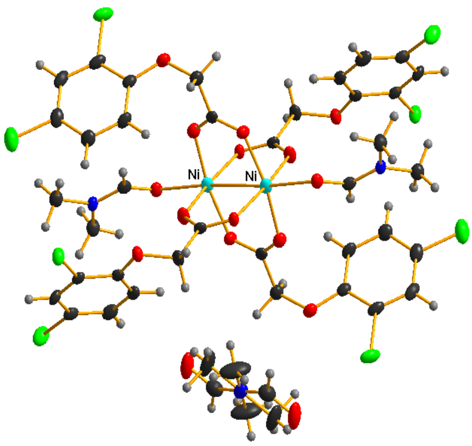


Fig. 12. Arrangement of molecules in the crystal of the complex compound $[Ni_2(2,4\text{-}D)_4(DMFA)_2]$.

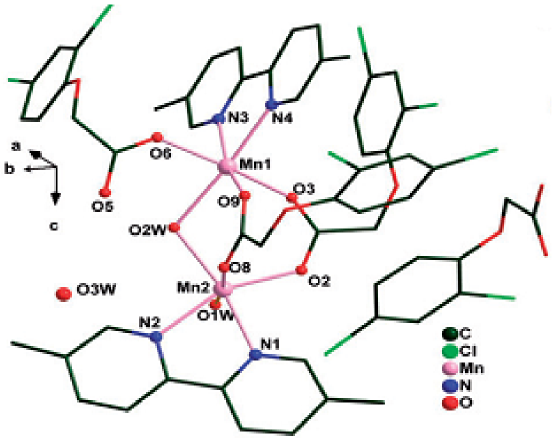


Fig. 13. [Asymmetric unit and 3-D structure of the complex compound Mn2(2,4-D)3$(DMPY)_2(\mu_2\text{-}H_2O)(H_2O)$]*(2,4-D)*0.2$(H_2O)$

As both ligands form a bridge, a double-stranded chain is formed. The complex is monoclinic, crystallized in space group R21/s, α=10.598(2)Å, β=18.552(3)Å, c=15.212(3)Å, β=108.835(2)°, V= 2830.9(8)Å3 , Z = 4 Figure 14. The tetrakis [(2,4-dichlorophenoxy)acetato] bis(2,2-bipyridylamine) di-copper(II) complex was crystallized in space group R1, its crystal cell sizes are as follows: α=10.813(1)Å, β=12.138(1)Å, c=11.909(1)Å, a=86.448(3)°, b=80.127(3)° and -=63.982(3)°, V=1383.7(2) Å3, Z=1.

To synthesize this complex, CH_3ONa (10 mmol) was added to a solution of 2,4-D (10 mmol) dissolved in methanol (50 mL), and after stirring for 30 min, $CuCl_2$-$2H_2O$ (5 mmol) and bipyridylamine (bipyam) dissolved in methanol (25 mL) were added. 10 mmol) was added dropwise. The reaction mixture was boiled for one hour. The volume of the blue solution was reduced by evaporation of the solvent and then allowed to slowly evaporate. Green prismatic $[Cu_2(2,4\text{-}D)4(bipyam)2]$ crystals suitable for RSA were grown for one week. It is soluble in DMFA, DMSO and pyridine. Synthesis reaction equation:

$C_6H_3Cl_2OCH_2COOH + CH_3ONa \rightarrow C_6H_3Cl \quad - OCH_2COONa$

$4C_6H_3Cl_2OCH_2COONa + 2CuCl_2 + 2bipyam \rightarrow$
$Cu_2(C_6H_3Cl \quad - OCH_2COO)_4(bipyam)_2$

Two bidentate carboxylate ligands formed syn-syn bridges between copper atoms at a distance of 4.50 Å. The other two carboxylate ligands are monodentately bonded to Cu(II) atoms, while the two neutral bipyam ligands are bidentately coordinated to copper atoms. The bridging ligands attached to two Cu(II) metal ions are asymmetric [Cu–O($_1$) = 1.963($_2$) Å, Cu–O($_2$) = 2.209(2) Å]. Each of the monodentate carboxylate ligands is connected to the Cu(II) ion through O(4) at a distance of 1.951(2) Å, and the non-coordinated carboxylate oxygen O(5) forms an N-bond through the NH group with the bipyam ligand adjacent to the molecule: [H($_2$)···O($_5$)=2.045 Å and N($_2$)···O($_5$)=2.797 Å], resulting in a polymer with an inter-dimer Cu···Cu distance of 6.46 Å. Each copper atom is five-coordinated, the other two positions are occupied by two nitrogen atoms N(1) and N(3) of bipyam molecule (1.984(2) and 2.027(2) Å) [30].

[Cd(2,4-D)$_2$(Im)2(H$_2$O)$_2$] complex containing 2,4-D and imidazole ligands was synthesized and characterized by elemental analysis, IR-spectroscopy and RSA methods. The Cd(II) atom has a distorted octahedral geometry and is coordinated with 2 O atoms of 2 monodentate 2,4-D ligands, 2 N atoms of 2 imidazole ligands, and 2 water molecules. Intermolecular O–H···O hydrogen bonds formed chains, and N–H···O hydrogen bonds formed a layered structure. Molecules formed a 2D supramolecular system due to p:::p interactions [31]. [Cd(2,4-D)$_2$(Im)2(H$_2$O)$_2$] complex is monoclinic and belongs to R21/s space group, α = 14.3069(12) Å, β = 12.7687(11) Å, c = 7.5954(7) Å, b =99.5910(10)°, V = 1368.1(2) Å3, Z = 2 in Figure 15.

To synthesize it, a mixture of Cd(NO$_3$)$_2$·4H$_2$O (0.5 mmol), 2,4-D (1.0 mmol), imidazole (1.0 mmol), NaOH (1.0 mmol) and H$_2$O (15 mL) was stirred in open air for 10 minutes. then placed in a Teflon-lined autoclave (25 ml) and kept at 120°C for 72 hours. Then, upon gentle cooling to room temperature, pale yellow block crystals suitable for RSA were obtainedin Figure 16. Mixed ligand coordination complexes of Zn(II), Cd(II) and Co(II) containing 2,4-D and imidazole derivatives [Cd$_2$(2,4-D)$_4$(PBIX)2], [Cd(2,4 -D)$_2$(OBIX)]n, [Zn(2,4-D)$_2$(OBIX)]n, [Co(2,4-D)$_2$(BIM)(H$_2$O)$_2$]n and [Cd(2 ,4-D)(NBI)]n were synthesized and their structure was studied by elemental analysis, IR-spectrum, RSA methods. According to RSA, the bimetallic Cd(II) subunit in the [Cd$_2$(2,4-D)$_4$(PBIX)$_2$] complex forms the 0D structure of a 26-membered metal-macrocycle with the help of PBIX bridges. [Cd(2,4-D)$_2$(OBIX)]n, [Zn(2,4-D)$_2$(OBIX)]n, [Co(2,4-D)$_2$(BIM)(H$_2$O)$_2$] In n complexes, metal centers bind to OBIX or BIM molecules and form a 1D chain (Figure 17, Table 3 and 4) [32].

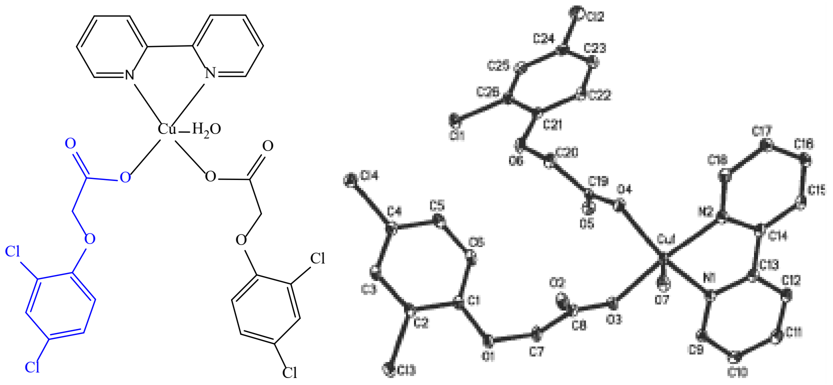


Fig. 14. Structures of the complex compound [Cu(2,4-D)$_2$(BP)H$_2$O].

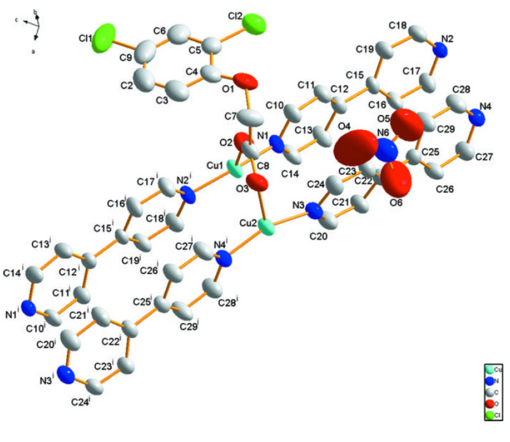


Fig. 15. Structures of the complex compound {[Cu$_2$(C$_8$H$_5$Cl$_2$O$_3$)(C$_{10}$H$_8$N$_2$)$_2$]NO$_3$}n.

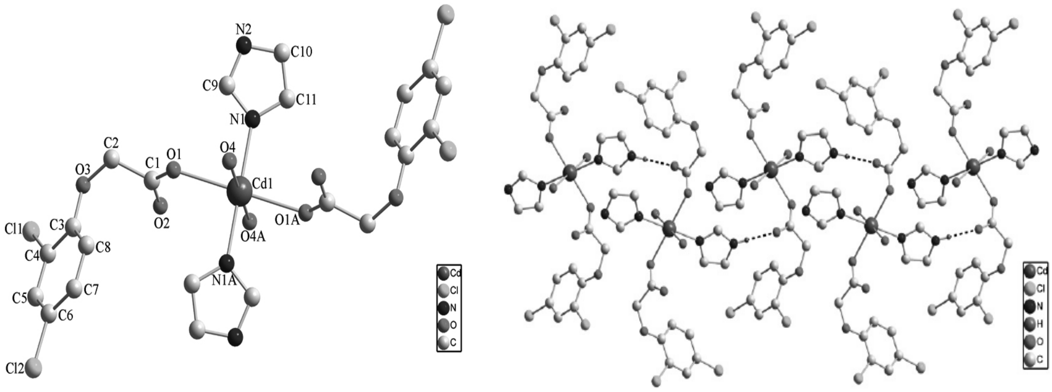


Fig. 16. Molecular structure of $[Cd(2,4\text{-}D)_2(Im)_2(H_2O)_2]$ complex and chain structure formed due to N–H···O hydrogen bonds

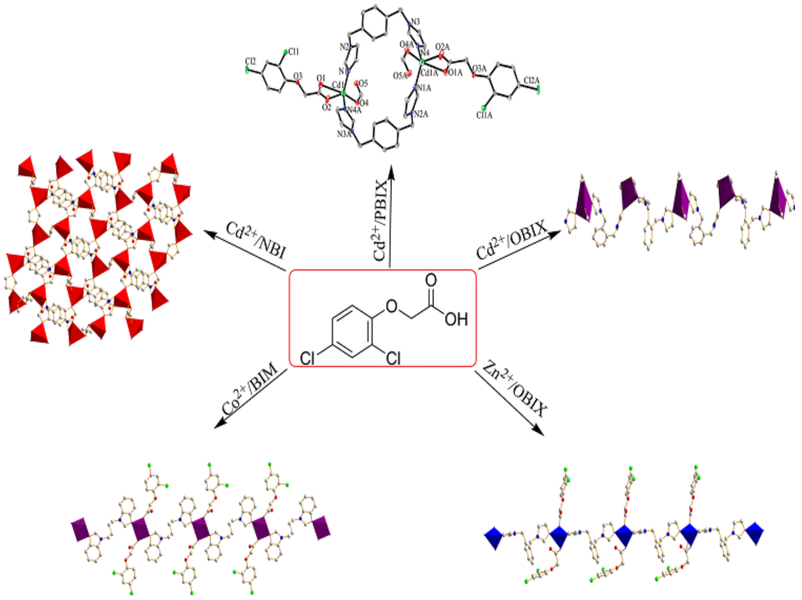


Fig. 17. $[Cd_2(2,4\text{-}D)_4(PBIX)_2]$, $[Cd(2,4\text{-}D)_2(OBIX)]n$, $[Zn(2,4\text{-}D)_2(OBIX)]n$, [Co Molecular structure of complex compounds (2,4-D)2(BIM)(H2O)2]n and [Cd(2,4-D)(NBI)]n

Table 3. Some bond lengths (Å) and angles (o) of $[Cd(2,4\text{-}D)_2(Im)2(H_2O)_2]$ complex

Cd1−O1	2.370(2)	C1−O1	1.244(4)
Cd1−O4	2.394(2)	C1−O2	1.249(3)
Cd1−N1	2.238(2)		
N1−Cd1− N1A	180.000(1)	N1−Cd1−O1A	93.09(8)
N1−Cd1−O1	86.91(8)	O1A−Cd1−O1	180.0
N1−Cd1−O4	92.37(9)	O1A−Cd1−O4	103.40(9)
N1−Cd1−O4A	87.63(9)	O4−Cd1−O4A	180.0

Table 4. Geometry of H-bonds in $[Cd(2,4\text{-}D)_2(Im)2(H_2O)_2]$ complex

D−H···A	**D−H[A]**	**H···A[A]**	**D···A[A]**	**D−H···A[°]**
N_2−H_2···O2^a	0.860	1.940	2.798	175.96
O_4−H_4C···O2^b	0.850	1.945	2.788	171.37

Symmetry code: (a) -x+1, y-1/2, -z+3/2; (b) -x+1, -y+1, -z+2

$[Cd_2(2,4\text{-}D)_4(PBIX)_2]$ complex is in a centrosymmetric dimer structure and consists of two Cd(II) atoms, four 2,4-D anions and 2 PBIX ligands. Each Cd(II) atom is five-coordinated: 3 oxygen atoms of 2 2,4-D anions and 2 nitrogen atoms of 2 PBIX ligands. So, the Cd(II) atom is located in a distorted trigonal bipyramid geometry, with a value of t 0.58 (t = 0 for a cubic pyramid, and t = 1 for a trigonal bipyramid). The Cd–O bond length is 1.929(8)–2.530(9) Å, and the Cd–N distance is 1.978(8)–2.006(9) Å. This is the same distance as in similar Cd(II) complexes. 2,4-D ligands exhibit 2 coordination natures. 2,4-D ligand forms a bidentate chelate with Cd(II) ions at the expense of O1 and O1A atoms in the carboxyl group, the torsion angle between C_1–C_2 and O_3–C_3 bonds is − 171.6(9)°; 2,4-D ligand is monodentately coordinated with Cd(II) ions due to O_4 and O_4A atoms in the carboxyl group, in this case the torsional angle between C_{11}–C_6 and C_{10}–C_9 bonds is − 60(1)°. These data demonstrate the remarkable conformational flexibility of the $–OCH_2COO–$ group toward rigid aromatic carboxylate ligands. Two PBIX ligands bridge two $[Cd(2,4\text{-}D)_2]$ moieties in the c-form (cis conformation) to form a dinuclear 26-membered metallo-macrocycle Figure 18.

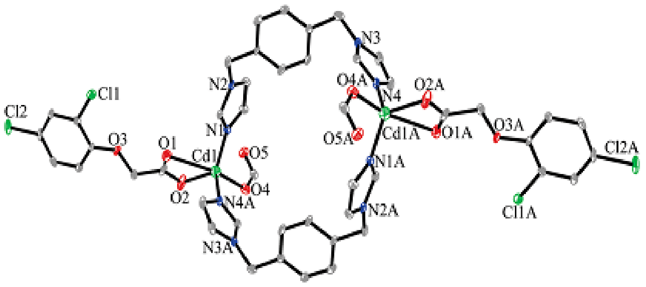
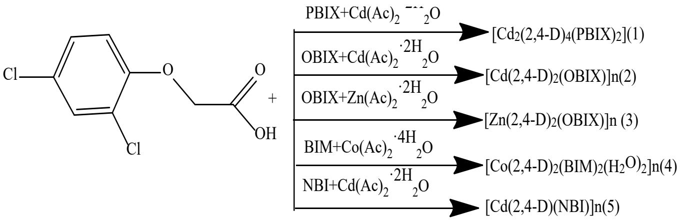


Fig. 18. Molecular structure of the complex [Cd2(2,4-D)$_4$(PBIX)$_2$].

The intramolecular Cd–Cd distance is 11.561(22) Å. The dihedral angles between the imidazole and phenyl rings are 71.83 and 84.01°, respectively. These binuclear metal-macrocycles are connected to each other through π–π interactions due to the phenyl groups of 2,4-D ligands, the centroid-centroid distance is 3.670 Å, and a 1D chain is formed in Figure 18 [31].

The synthesis scheme of complex compounds with imidazole-derivatives is as follows in Scheme 6:



Scheme 6. The synthesis scheme of complex compounds with imidazole-derivatives

The $[Zn(2,4\text{-}D)_2(OBIX)]_n$ complex was crystallized in the triclinic P-1 space group. The asymmetric unit contains one Zn(II) atom, two 2,4-D anions, and one OBIX ligand (Figure 19a).

Two nitrogen atoms of two OBIX molecules are attached to the Zn(II) center, the Zn–N bond length is 1.989(3)–1.995(3) Å and the N(1)–Zn–N(1A) bond angle is 118.74(14)°. The remaining parts of the coordination cell are filled by 2 2,4-D anion carboxyl group oxygen atoms, which are monodentate, and the Zn–O bond length is 1.945(3)–1.957(3) Å. In the $[Zn(2,4\text{-}D)_2(OBIX)]_n$ complex, OBIX is in the trans conformation, the $N_1 \cdots N_4$ distance is 8.885 Å, and the dihedral angles between the imidazole and phenyl rings are 66.78 and 70.68°, respectively.

Each OBIX ligand participates as a bis-linker, which forms a bridge between adjacent Zn(II) ions, forming a 1D chain, with a Zn···Zn distance of 12.124 Å Figure 19b.

$[Co(2,4\text{-}D)_2(BIM)(H_2O)_2]_n$ complex was isolated from the reaction of 2,4-DH, BIM and $Co(OAc)_2 \cdot 4H_2O$. The asymmetric unit of the complex contains one Co(II) atom, two 2,4-D anions, one BIM molecule and two water molecules. The central Co(II) atom is in distorted octahedral coordination: 4 oxygen atoms of two 2,4-D anions (O_3, O_3A, O_4 and O_4A), 2 water molecules with Co–O distances from 2.100(12) to 2.151(13) Å, 2 nitrogen atoms (N1 and N1A) of BIM ligand with Co–N distance of 2.140(15) Å. The Co–O/N bond lengths are normal Figure 20.

The flexible BIM ligand is in the trans conformation, with a dihedral angle of 0.215° between the 2 benzimidazole rings. BIM ligands bridge neighboring Co(II) atoms and form a 1D chain along the β axis, with a Co···Co distance of 12.3508 Å. 2,4-D ligands are in monodentate coordination and bind to the 1D chain from both sides Figure 21.

Synthesis of $[Cd_2(2,4\text{-}D)_4(PBIX)_2]$ complex. A mixture of $Cd(OAc)_2 \cdot 2H_2O$ (26.6 mg, 0.1 mmol), 2,4-DH (22.1 mg, 0.1 mmol), PBIX (24.2 mg, 0.1 mmol) and water (10.0 mL) was placed in a steel vessel and heated at 120°C. heated for 3 days at room temperature. After cooling to room temperature at a rate of 5°C/h, colorless blocky single crystals were obtained in 43% yield (17.0 mg). Analytical calculated for $C_{60}H_{48}N_8O_{12}Cd_2$: C, 45.53; H, 3.04; N, 7.08. Found: C, 45.49; H, 3.00; N, 7.15. IR spectrum (KBr, cm−1): 3132, 1652, 1411, 1360, 1215, 1031, 789, 635. Fluorescence in the solid state (λemission = 475 nm, λexcitation = 378 nm) [32].

The complex $[Zn(2,4\text{-}D)(isonicotinate)]_n$ was synthesized under hydrothermal conditions, its structure was studied by elemental analysis, IR-spectroscopy, thermogravimetric analysis and X-ray diffraction in Figure 22.

The complex was formed under solvothermal conditions. Copper(II) nitrate trihydrate (0.06 g, 0.25 mmol), 2,4-D (0.11 g, 0.5 mmol), pyrazine (0.04 g, 0.5 mmol), and acetonitrile (10 mL) were placed in a Teflon-lined steel vessel and heated at 353 K. heated for 3 days, then slowly cooled to room temperature, resulting in the formation of green single crystals [33]. Crystals of the complex belong to space group R1, a=9.8662(3) Å, b=10.9610(4) Å, c=11.0262(5) Å, a=63.467(2)o, b=78.764(2)°, g=72.87692)o, V=1016.73 Å3, Z=1 in Figure 23.

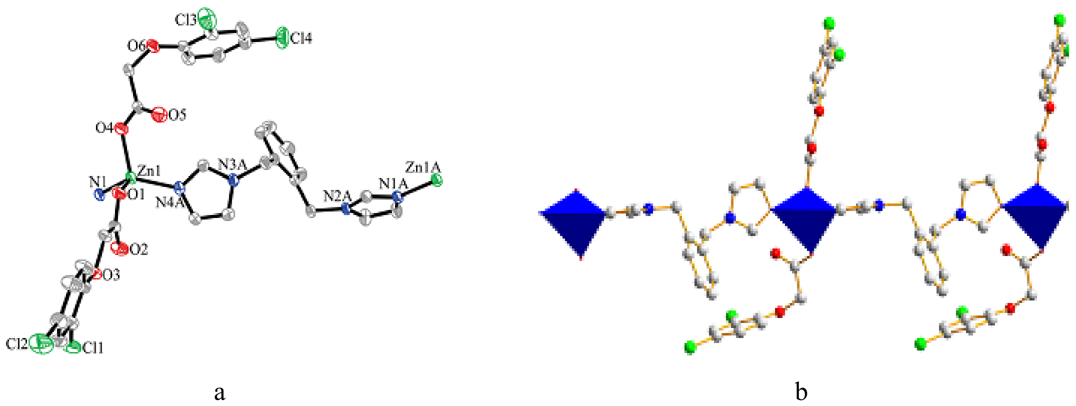


Fig. 19. Molecular structure of [Zn(2,4-D)$_2$(OBIX)]n complex compound (a) and 1D chain formation (b

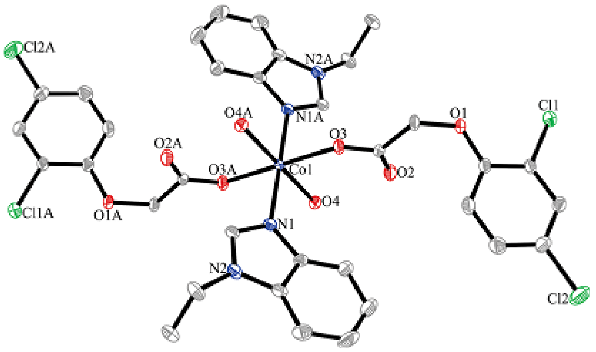


Fig. 20. Molecular structure of the complex compound [Co(2,4-D)$_2$(BIM)(H$_2$O)$_2$]n

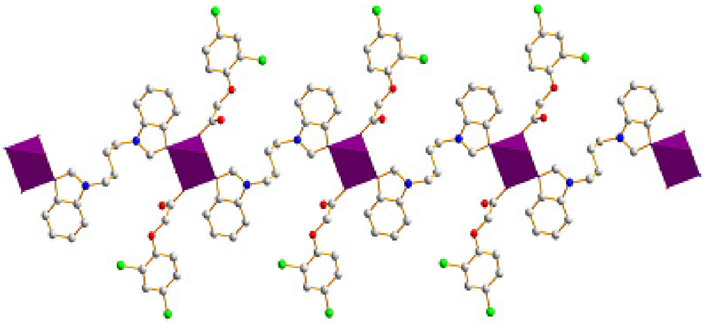


Fig. 21. 1D chain formation of complex compound [Co(2,4-D)$_2$(BIM)(H$_2$O)$_2$]n

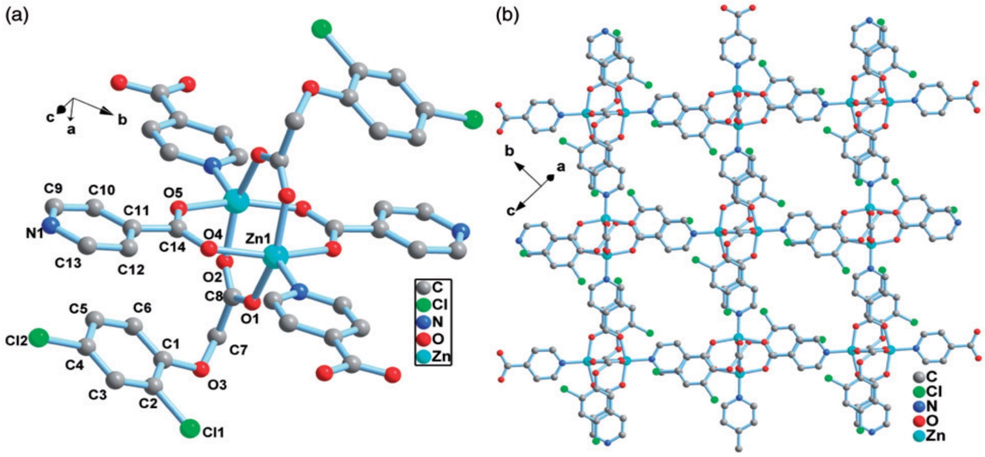


Fig. 22. Molecular deposition of [Zn(2,4-D)(isonicotinate)]n complex compound (a) and formation of a 2-D system chain (b)

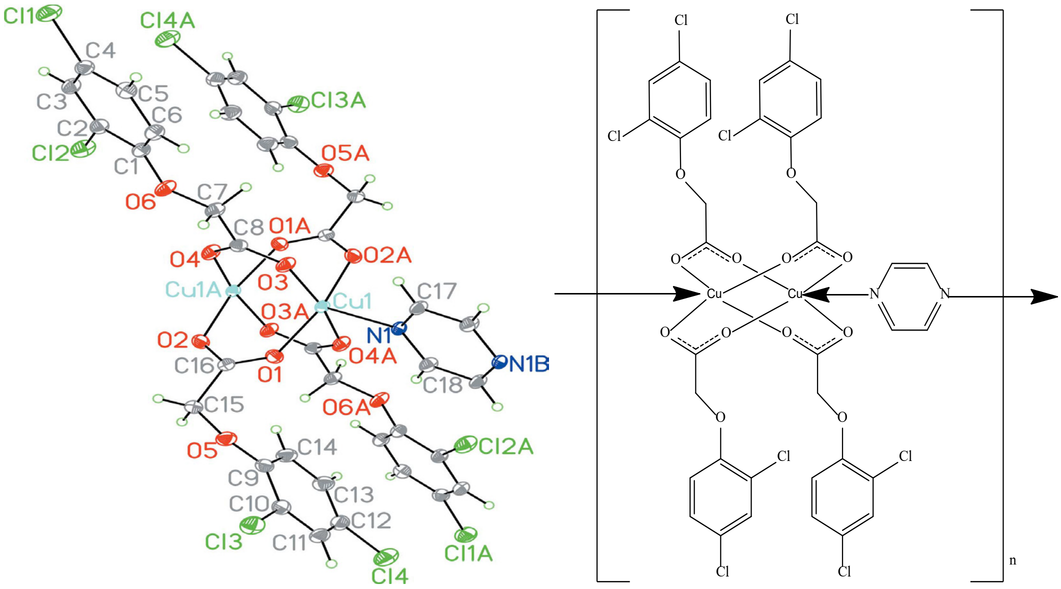


Fig. 23. Molecular structure of the complex compound [Cu_2(2,4-D)$_4$($C_4H_4N_2$)]n

In the chain structure of [Cu_2(2,4-D)$_4$($C_4H_4N_2$)]n complex, tetrakis(2,4-D)-di-copper(II) and pyrazine units appear alternately, square pyramidal copper(II) centers are 4 in turn bound to a bridging 2,4-D anion and a single bridging pyrazine molecule. Both the dinuclear copper moiety and the pyrazine ligand have a center of symmetry [33].

The asymmetric unit has half of [Cu_2(2,4-D)$_4$($C_4H_4N_2$)]n and the other half has a pyrazine ligand. A complete dinuclear unit and pyrazine are formed by the inversion center. The square-pyramidal coordination geometry of the copper(II) atom is formed by the 4 main O atoms of the 4-bridged 2,4-D anion and the apical N atom of the single-bridged pyrazine molecule.

3. Biological activity of phenoxyacetic acid derivatives

One of the urgent problems in world agriculture is to obtain low-toxicity and high-efficiency stimulants that increase plant productivity and fight against various harmful insects and phytopathogenic microorganisms. The entire life of plants, that is, from the development of the fertilized egg cell to the aging of the organism, all the processes take place with the participation of phytohormones. During all phases of cell development, chemical information is exchanged in plant tissues and organs, and by chemical definition, more interaction takes place. For this, they produce special chemicals called phytohormones. These substances are involved in the processes of plant growth, formation of new organs, flowering, aging of leaves. Phytohormones ensure the proper functioning of certain parts of the plant organism and its functional integrity. Until now, a number of families of phytohormones performing certain functions in the plant organism have been identified: auxins, gibberellins, cytokinin, ethylene, abscisic acid. Auxin is considered a plant growth regulator and was isolated from plants [34, 35].

The founder of the first selective herbicides was indolylacetic acid, discovered by Fritz Kogl. By the beginning of the Second World War, basic university science found that not only this substance, but also other derivatives of acetic acid have the properties of plant hormones-auxins (from the Greek for growth) [36]

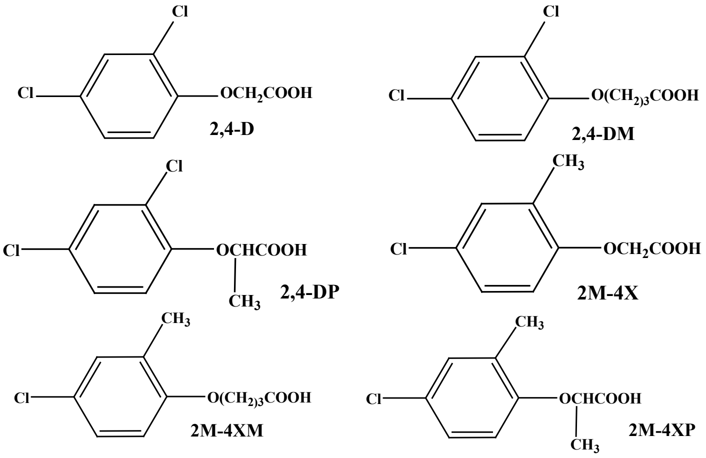
The halogenated derivatives of phenoxyacetic acids, 2,4-D (US) and 2-methyl-4-chlorophenoxyacetic acid (UK), were developed in the 1940s in the US and UK. Widespread after World War II, they revolutionized weed control as selective herbicides with the ability to selectively kill perennial broadleaf weeds without harming cereals and other grasses [37].

Zimmerman and Hitchcock found that chlorinated phenolacetic acids had high auxin activity. Among them, 2,4-dichlorophenoxyacetic acid, synthesized by Pokorny a year earlier, became of special importance. The main difference between 2,4-D and other organochlorine compounds used as pesticides in agriculture is that it undergoes relatively rapid transformation in plants and is non-toxic. As soon as the herbicidal properties of 2,4-D were discovered, it was found that it undergoes decarboxylation in plants with the release of carbon dioxide gas into the atmosphere. Carbon dioxide can participate in the process of substance exchange in the plant organism [38, 39]. It turns out that the process of decarboxylation with oxidation is somewhat difficult and takes place in different schemes.

The physiological activity of phenols is significantly higher than that of alcohols. They have herbicidal, fungicidal, insecticidal and bactericidal properties. The introduction of halogen, nitro-, thiocyanate, alkyl groups into the aromatic ring increases their pesticidal activity. An increase in the alkyl radical chain also leads to an initial increase in pesticide activity, then a decrease. Alkylphenols containing C_4 and C_5 alkyl groups have been found to have the highest herbicidal activity.

Regulator-type herbicides are derivatives of aryloxyalkylcarboxylic acids that have hormonal functions similar to those of indolylacetic acid. When a plant is treated with such hormonal preparations, an imbalance of phytohormones occurs, the normal development of the plant is disturbed, it dies due to lack of moisture and nutrients. The inclusion of halogen atoms in the composition of phenoxyacetic acid increases their physiological activity. Also, their activity depends on the position of the halogen atoms in the aromatic ring and increases in the following order for dichlorinated derivatives: 2,6-<3,5-<3,4-<2,5- 2,4-

Derivatives of 2,4-Dichlorophenol or 2-methyl-4-chlorophenol (2,4-D, 2,4-DM, 2,4-DP, 2M-4X, etc.) belong to this type of herbicides. They contain residues of acetic, propionic and fatty acids. They are harmless to mammals.



Scheme 7. Derivatives of 2,4-Dichlorophenol or 2-methyl-4-chlorophenol

Most of these types of herbicides are used as herbicides at concentrations of 0.01%, and at concentrations less than 0.001%, they have a growth effect [40].

2,4-D is widely used in agricultural practice to grow grain crops (wheat, barley, oats, corn, rice, buckwheat). The herbicide has a selective effect and causes the death of broad-leaved plants. Due to the special anatomical structure of the leaf plate (vertical location, less growth, high wax content), the herbicide exhibits weak sorption capacity, does not stick to the leaf surface. In addition, cereal plants are able to delay the action of the herbicide in the leaf by absorbing it on certain substrates, forming complexes with proteins. [41].

A simple technological process, the availability and cheapness of raw materials led to the large-scale production and long-term use of herbicide preparations based on 2,4-D. The production of commercial drugs with the active ingredient 2,4-D is currently not regulated by patents, so the volume of production is quite high and is represented on the market by a wide variety of trademarks, including combination drugs [42].

The amount of herbicide in preparations is up to 600 g/l. In agriculture, herbicides containing 2,4-D acid are widely used, including: Dikopur F, Aminka, Estet, 2,4-Daktiv, Elant, Zernomax, Octigen, Metis, Duplet Grand, Avrorek and other trademarks [43].

Research on the development of combined herbicide preparations with a synergistic active content of several active substances with different mechanisms of action is ongoing. Such compositions have high selective activity against various types of weeds in the studied crops, while reducing the ecological consequences of their use due to the low dose of each active substance in the preparation form. The following Eurasian patents are examples of such compositions:

1) synergistic composition of dicamba, clopyralid and picloram to control the harmful quarantine weed creeping mustard (pink) (Acroptilon repens) [44];

2) composition of ethametsulfuron-methyl and picloram for weed control in spring and winter rape crops [45];

3) synergistic composition of chlorimuron-ethyl, imazamox and arabinogalactan for weed control in soybean [46].

The effectiveness of combined herbicides based on 2,4-D was analyzed under different conditions of zonal application. The effect of application periods and composition of herbicides for oilseeds on the efficiency and yield of winter rape was studied [47]. The use of herbicides in soybean crops has been described [48]. V.Z. Venevtsev, M.N. Zakharova's scientific research studies in the Ryazan region, when studying the efficiency of using herbicides in soybeans, high efficiency was observed [49].

In the scientific works of M. Stasiewiez, A. Trugata, salts of alkyltrimethylammonium halogenated herbicide acids with improved wettability were obtained to reduce the toxicity of 2,4-D and other herbicide phenoxyacids to grain crops, which allows to reduce the dosage of drugs during processing [50-55].

A comprehensive review of the work on the adsorption and degradation of herbicides belonging to the class of phenoxyacetic acids in soil was compiled [56-61]. Adsorption of 2,4-D to soil components under oxidizing and non-oxidizing conditions was studied. It has been shown that 2,4-D is preferentially sorbed under oxidizing conditions and sorption is stronger in soils with high iron content [62-68].

4. Comparative Analysis

A systematic comparison of metal complexes derived from 4-chlorophenoxyacetic acid (4-D) and 2,4-dichlorophenoxyacetic acid (2,4-D) reveals clear structure–directing trends governed by the nature of the metal ion, ligand substitution pattern, and auxiliary donors. Across the reported complexes, monodentate coordination of the carboxylate group predominates

(~90%), particularly for 2,4-D derivatives, which can be rationalized by steric hindrance imposed by the ortho-chloro substituent that limits the formation of stable chelate rings. Transition metals such as Ni(II), Co(II), and Fe(II) preferentially adopt octahedral geometries, typically coordinated by two monodentate carboxylate oxygen atoms from the phenoxyacetate ligands and additional aqua or N-donor ligands. In contrast, Cu(II) complexes frequently display distorted square-pyramidal or elongated octahedral environments, with significantly lengthened axial Cu–O bonds (up to ~2.36 Å), reflecting the Jahn–Teller effect characteristic of the d^9 electronic configuration. Zn(II) complexes show a marked preference for tetrahedral coordination (CN = 4), as observed in $[Zn(2,4\text{-}D)_2]_n$ and mixed-ligand systems with ethylenediamine or imidazole derivatives. This behavior is consistent with the d^{10} electronic configuration of Zn(II), which lacks ligand field stabilization in octahedral fields and therefore favors lower coordination numbers. By contrast, Ni(II) (d^8) and Co(II) (d^7) benefit from higher LFSE in octahedral environments, explaining the observed geometry divergence. Bond length analysis further supports ionic radii and electronic effects: typical Ni–O distances (~2.04–2.08 Å) are shorter than the elongated axial Cu–O bonds (~2.30–2.36 Å), while Cd–O bonds are significantly longer (~2.27–2.53 Å), reflecting the larger ionic radius of Cd(II). These trends correlate well with periodic properties of the metal ions. From a crystallographic perspective, monoclinic space groups, particularly $P2_1/c$, dominate (~70% of reported structures). This preference can be attributed to favorable π–π stacking interactions between chlorinated phenyl rings and hydrogen-bonding networks involving coordinated and lattice water molecules, which stabilize inversion-related molecular packing motifs. Overall, the comparative analysis highlights how subtle variations in metal electronic configuration and ligand steric demand govern coordination number, geometry, dimensionality (0D to 2D/3D), and supramolecular assembly in phenoxyacetate complexes (Table 5).

5. Conclusions

From the analysis of the studied literature, it became clear that 4-chloro- and 2,4-dichlorophenoxyacetic acid derivatives are used for many purposes, and the oxygen atom in the carboxyl group is coordinated with the donor atoms in monodentate, bidentate, various bridges or chelated states, the occurrence of weak interactions, the main chemistry in general provides excellent performance as a ligand. The flexibility of the structure, ease of preparation and low cost make it possible to use such molecules in the formation of various complex compounds with the given properties in the presence of a number of intermediate d-metals.

At the same time, it is desirable and priority to continue research in the following directions:

1. Expanding the scope of using Me(II) and 4-D and 2,4-D systems in the synthesis process in order to obtain mixed coordination chelates, that is, different coordination modes, nuclear and magnetic properties depending on different metal sources, mixed metal systems or different synthesis conditions manageable;
2. Further optimization of the characteristic properties of complex compounds based on 4-chloro- and 2,4-dichlorophenoxyacetic acid; and this is achieved by clarifying and improving factors such as coordination environment, metal type and geometry. Also, more inorganic reactions, including asymmetric fields, can be studied more widely.

Table 5. Comparative summary of reported metal complexes of 4-D and 2,4-D

Metal ion	Ligand	Auxiliary ligand(s)	Coordination number (CN)	Geometry	Coordination mode of phenoxyacetate	Representative M–O bond length (Å)	Space group	Dimensionality	Key feature / remark	Ref.
Zn(I)	2,4-D	en	4	Tetrahedral	Monodentate	Zn–O ≈ 1.94	P2/c	0D(mononuclear)	d^{10}, prefers CN=4	[69-72]
Zn(II)	2,4-D	–	4	Tetrahedral	Monodentate/bridging	Zn–O ≈ 1.95–2.00	$P2_1/c$	1D polymer	Steric control by ortho-Cl	[73, 74]
Ni(II)	2,4-D	H_2O, N-donor	6	Octahedral	Monodentate	Ni–O ≈ 2.03–2.08	$P2_1/c$	0D/1D	High LFSE (d^8)	[75-77]
Co(II)	2,4-D	H_2O	6	Octahedral	Monodentate	Co–O ≈ 2.05–2.15	$P2_1/c$	0D/1D	d^7, octahedral favored	[78-86]
Cu(II)	2,4-D	H_2O, N-donor	5–6	Square-pyramidal / elongated octahedral	Monodentate	Cu–O(eq) ≈ 1.95–2.00; Cu–O(ax) ≈ 2.30–2.36	$P2_1/c$	0D/1D	Jahn–Teller distortion (d^9)	[87, 88]

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Data Availability

The data supporting the findings of this study are available within the manuscript. Additional data may be available upon request from the corresponding author.

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